

REMARKS

Summary of Changes Made

The Application was filed with 44 claims, claims 5-7, 20-27, 29-31, 39 and 41 were previously canceled, and claims up to 53 were previously added, while claims 46-53 were withdrawn as drawn to non-elected inventions. New claim 54 is added herein.

Accordingly, claims 1-4, 8-19, 28, 32-38, 40, and 42-54 (38 claims) remain pending, while all of the foregoing except claims 46-53 remain under consideration. Applicants expressly acknowledge that claims 28 and 42-45 are part of Group I and are being examined. No new matter is added by this amendment.

Claim Rejections – 35 U.S.C. 102 or 103 – (Branagan)

Claims 1-4, 8-14, 17-19, 28, 40, and 42-45 are rejected under 35 U.S.C. 102(b) and/or 103(a) as anticipated and/or obvious in view of Branagan et al., XP-002556375, Wear-Resistant Amorphous and Nanocomposite Steel Coatings, (“Branagan”).

As explained below, Branagan fails to disclose a thermal sprayed coating layer of a metallic glass of which the supercooled liquid temperature range ΔT_x is 30 °C or more.

Metallic Glass (Glass Alloy). A most remarkable feature of metallic glass is that metallic glass exhibits a distinct glass transition and a wide supercooled liquid temperature range before crystallization when heated. See [0032] of the specification.

The thermal sprayed coating layer of the present invention is a metallic glass (glass alloy) having supercooled liquid temperature range ΔT_x of 30 °C or more.

The glass transition temperature (T_g), the crystallization initiation temperature (T_x) and the supercooled liquid temperature range ΔT_x ($\Delta T_x = T_x - T_g$) can be measured by DSC, DTA or the like. In the measurement, ΔT_x is shown as a broad and wide endothermic band before the crystallization initiation temperature T_x . The ΔT_x of a glass alloy is very wide, such as 10-130 °C. On the other hand, when a conventional amorphous alloy is heated, it does not exhibit a glass transition and the ΔT_x is approximately zero. See [0007] and [0030]-[0033] of the specification.

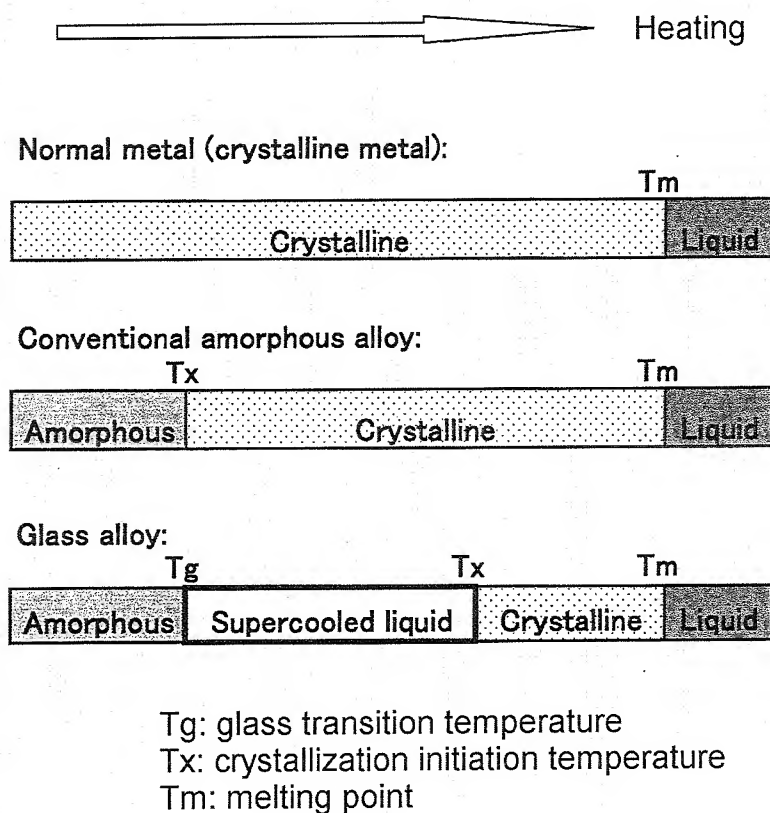
The following FIG-I schematically shows the phase transformation behaviors of a normal metal (crystalline metal), a conventional amorphous alloy, and a glass alloy when they are heated.

When a normal metal (crystalline metal) is heated, the crystalline becomes the melt at the melting point T_m .

When a conventional amorphous alloy is heated, the amorphous is crystallized at the crystallization temperature T_x , and then melted at the melting point T_m .

In contrast, when a metallic glass (glass alloy) is heated, the amorphous becomes supercooled liquid state at the glass transition temperature T_g , and after that, crystallized at the crystallization temperature T_x , and finally melted at the melting point T_m .

FIG-I:



Thermal Sprayed coating of Metallic Glass. As defined in claim 46 (withdrawn claim), the thermal spray coating of metallic glass of the present invention can be produced by thermal spraying amorphous metallic glass powder on the substrate surface, wherein:

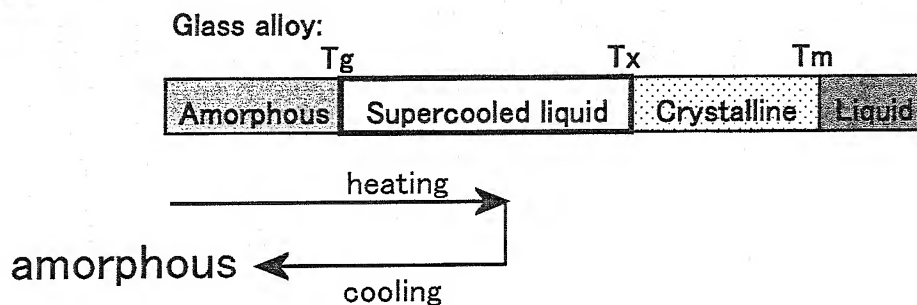
(i) amorphous metallic glass powder having ΔT_x of 30 °C or more is used as a material to be thermal sprayed;

(ii) the amorphous metallic glass powder is heated to a temperature below T_x (i.e., without being melted) and converted into a supercooled liquid state; and

(iii) then the powder in supercooled liquid state is deposited and solidified on the substrate to form the coating.

When the amorphous metallic glass being converted into a supercooled liquid state without being melted is cooled, it always cooled without passing through the crystallization initiation temperature T_x and, therefore, it will inevitably return to the previous state (amorphous solid) independent of the cooling rate as following FIG-II. See [0045] of the specification: "If the metallic glass is heated to the temperature range that is below the crystallization starting temperature, it safely solidifies to an amorphous state without a large influence of the cooling rate."

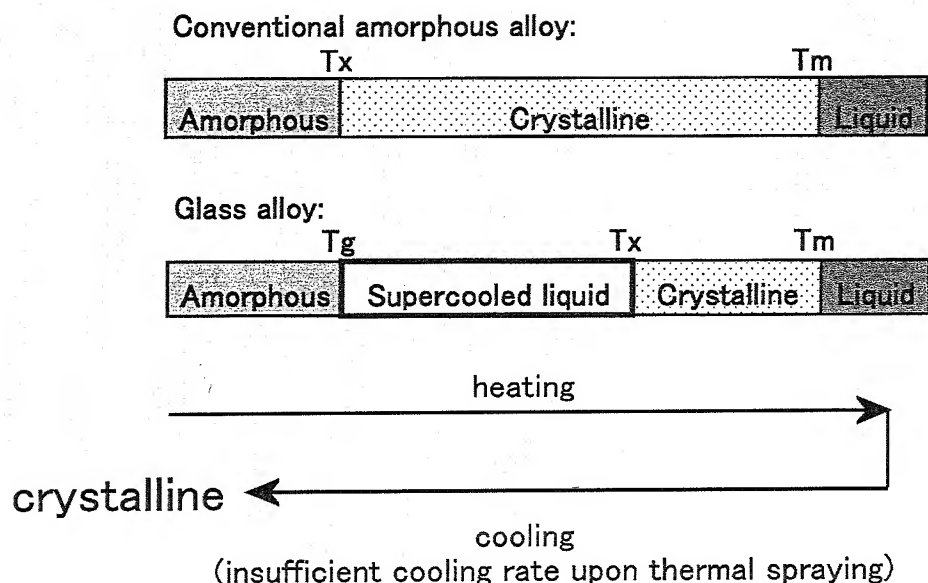
FIG-II:



On the other hand, when the melted metallic glass is cooled, it always cooled with passing through T_x . If the temperature slowly rises through the crystallization temperature, the melt is crystallized. In other words, if the metallic glass powder is heated to be melted and then cooled, the structure of the resulting coating is significantly affected by the cooling rate.

In thermal spraying, the substrate surface to be coated is repeatedly and remarkably heated by the flame of thermal spraying and numerous high-temperature sprayed particles. Therefore, it is very hard to cool the melt with rapid cooling rate enough to avoid crystallization as shown in FIG-III.

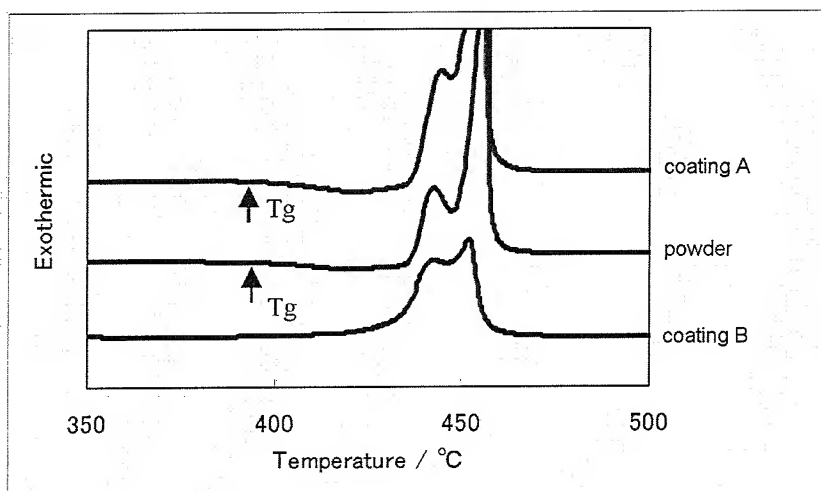
FIG-III:



In addition, when the metallic glass powder is melted through thermal spraying, the property such as T_g , T_x or ΔT_x of obtained thermal sprayed coating is more easily differentiated from the previous metallic glass due to melting with high heat load, and as the result, the desired thermal sprayed coating (i.e., the coating having the property same as that of starting metallic glass powder) can not be obtained. The reason is considered that the composition of the coating may varies due to crystallization, oxidation, volatilization, etc through thermal spraying to melt the powder material with high heat load.

The FIG-IV shows DSC measurement result of an amorphous metallic glass powder $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ ($T_g = 396.6^\circ\text{C}$, $T_x = 436.2^\circ\text{C}$, $T_m = 980^\circ\text{C}$) and thermal spray coatings obtained by thermal spraying the powder. The coating A was obtained by thermal spraying without melting the powder according to the present invention, and the coating B was obtained by thermal spraying with melting the powder in a higher heat load condition than that of coating A.

FIG-IV:



	Tg	Tx
powder	396.6°C	436.2°C
coating A	393.2°C	436.7°C
coating B	N.D.	433.1°C

As is clear from FIG-IV, there is no difference in DSC between the coating A and the powder and therefore the coating A has the same property as the powder. However, the coating B is different in DSC from the powder (i.e., disappearance of Tg and ΔT_x , and change in the peak shape): this means that the composition of coating B is different from that of the powder due to melting of the powder through thermal spraying.

Thus, by thermal spraying wherein the powder material is melted, it is extremely hard to obtain a thermal sprayed coating having the same composition and property as the amorphous metallic glass powder used as a starting material to be sprayed.

Branagan's thermal sprayed coating. For HVOF and plasma spraying, Branagan uses steel alloy powder of $\text{Fe}_{63}\text{Cr}_8\text{Mo}_2\text{B}_{17}\text{C}_5\text{Si}_1\text{Al}_4$. From Fig. 9, the powder seems to have Tg and Tx, but both HVOF coating and plasma sprayed coating do NOT have Tg and ΔT_x . In addition, Tx of the HVOF coating and Tm of the plasma sprayed coating is clearly different from those of the powder.

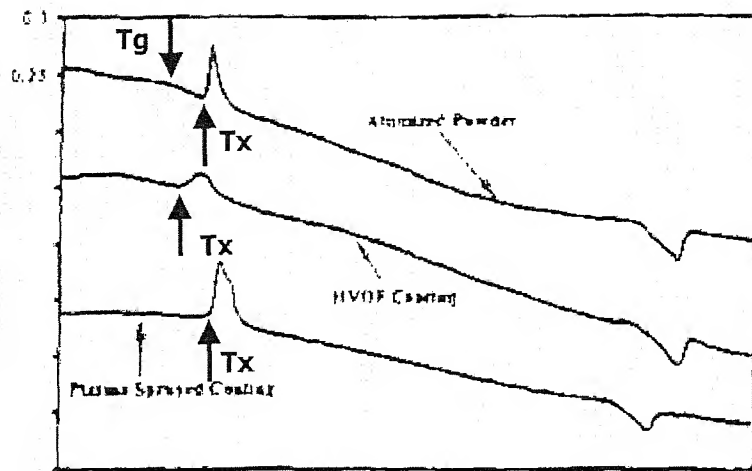


Fig. 9.—DTA scans of the air-classified powder, the as-deposited plasma coating, and the as-deposited HVOF coating

This suggests that the powder may be a metallic glass, but the composition and property of HVOF and plasma sprayed coatings are different from the powder and the coatings are no longer metallic glass.

Therefore, Branagan does NOT disclose a thermal sprayed coating layer of a metallic glass having ΔT_x of 30 °C or more.

The examiner said that “Branagan is considered to meet the recited method limitations wherein deposition occurs in supercooled liquid state and via a thermal spraying method.”

Branagan discloses that the glass % in HVOF coating is similar to that in the powder and the glass % in plasma coating is significantly different from that in the powder and, therefore, infers the powder is melted through plasma spraying, while the powder is not melted through HVOF (p.2619, left column, 1st paragraph and p.2620, right column, 2nd paragraph).

However, as is clear from Fig. 9, both coatings of Branagan is clearly different in the thermal behavior from the starting powder and, therefore, it is reasonably considered that the powder is heated to be melted through HVOF and plasma spraying in Branagan.

Based on the foregoing, claims 1-4, 8-14, 17-19, 28, 40, and 42-45 are both novel and non-obvious over Branagan.

Claim Rejections – 35 U.S.C. 103 – (Branagan)

Claims 15, 16 and 32-38 are rejected under 35 U.S.C. 103(a) as obvious in view of Branagan.

With respect to these dependent claims, Applicants have amply demonstrated the patentability of the claims from which they depend, above. Examiner is respectfully requested to acknowledge the patentability of claims 15, 16, and 32-38 on that basis.

New Claim

New claim 54 is added herein, which claims “[t]he metallic glass laminate according to claim 1, wherein the thermal sprayed coating layer of metallic glass has crystallization degree of 10% or lower.” Such limitation is found in paragraph [0050] of the specification.

Claim 54 is patentable over Branagan as the reference discloses that the HVOF coating is 41% glass (i.e., 59% crystalline) and the plasma spray coating is 86% glass (i.e., 14% crystalline).

Entry of claim 54 and indication of its allowability are respectfully requested.

CONCLUSION

In light of the foregoing, it is respectfully submitted that the present application, including claims 1-4, 8-19, 28, 32-38, 40, and 42-45, is in condition for allowance and notice to that effect is hereby requested. If it is determined that the application is not in a condition for allowance, the Examiner is invited to initiate a telephone interview with the undersigned attorney to expedite prosecution of the present application.

If there are any additional fees resulting from this communication, please charge the same to our Deposit Account No. 18-0160, our Order No. IWI-16783.

Respectfully submitted,

RANKIN, HILL & CLARK LLP

/ Christopher J. Korff /
Kenneth A. Clark
Reg. No. 32,119
Christopher J. Korff
Reg. No. 55,342

23755 Lorain Road - Suite 200
North Olmsted, 44070-2224
(216) 566-9700
docketing@rankinhill.com